Achieving High Dielectric Constant and Low Loss Property in a Dipolar Glass Polymer Containing Strongly Dipolar and Small-Sized Sulfone Groups

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ABSTRACT: In this report, a dipolar glass polymer, poly(2-(methylsulfonyl)ethyl methacrylate) (PMSEMA), was synthesized by free radical polymerization of the corresponding methacrylate monomer. Due to the large dipole moment (4.25 D) and small size of the side-chain sulfone groups, PMSEMA exhibited a strong γ transition at a temperature as low as −110 °C at 1 Hz, about 220 °C below its glass transition temperature around 109 °C. Because of this strong γ dipole relaxation, the glassy PMSEMA sample exhibited a high dielectric constant of 11.4 and a low dissipation factor (tan δ) of 0.02 at 25 °C and 1 Hz. From an electric displacement-electric field (D-E) loop study, PMSEMA demonstrated a high discharge energy density of 4.54 J/cm³ at 283 MV/m, nearly 3 times that of an analogue polymer, poly(methyl methacrylate) (PMMA). However, the hysteresis loss was only 1/3−1/2 of that for PMMA. This study suggests that dipolar glass polymers with large dipole moments and small-sized dipolar side groups are promising candidates for high energy density and low loss dielectric applications.

KEYWORDS: dipolar glass polymer, orientational polarization, sub-Tg transition, dielectric constant, broadband dielectric spectroscopy, electric energy storage

1. INTRODUCTION

Polymer dielectrics are important materials for advanced electrical and power applications.1,2 With the development in power electronics such as electric motors for electrical and hybrid electric vehicles, next-generation polymer dielectrics with high energy density, high temperature capability, as well as low dielectric loss are highly desirable. For linear dielectric polymers, the energy density can be calculated as

\[ U_e = 0.5k\varepsilon_0E^2, \]

where \( k \) is the relative dielectric constant, \( \varepsilon_0 \) the vacuum permittivity, and \( E \) the applied electric field.3 To increase electric energy storage, increasing breakdown strength seems to be more attractive than increasing dielectric constant, because \( U_e \) scales as the second power of the electric field. However, it is fairly difficult to substantially increase the breakdown strength for polymer films because of two reasons. First, the highest electrical breakdown strength is observed for inorganic single crystals, such as diamond, around 2 GV/m.4 Current state-of-the-art polymer dielectric material, such as biaxially oriented polypropylene (BOPP), has already reached a breakdown strength of 730 MV/m.5 It is difficult to further enhance electrical breakdown strength for polymers. Second, the much lower engineering breakdown strength than the intrinsic breakdown strength6 (around 10 GV/m) at a band gap of 8 eV (e.g., for polyethylene7) must originate from impurities and manufacturing defects in polymer films. Therefore, it is more practical to increase the dielectric constant, rather than electrical breakdown strength. This requires us to understand the fundamental polarization mechanisms in organic polymers.

As we know, there are five types of polarization for polymers, namely, electronic, atomic (or vibrational), orientational (or dipolar), ionic, and interfacial polarization.2,8,9 Electronic and atomic polarizations occur at very high frequencies, namely, in the infrared and optical ranges.8,9 It is the most desired to utilize both polarizations to increase dielectric constants of polymers because they show no losses in the power and radio frequencies. However, a recent computational study showed that only limited increases in dielectric constant could be achieved without significantly decreasing the band gap of polymers.10 For example, the dielectric constant for carbon-based polymers was limited to 4 and 7 for the band gap being 5
and 3 eV, respectively. On the other hand, interface and ionic polarizations are not desirable for film capacitor applications because they involve slow discharge processes and their dielectric losses are relatively high. This leaves only the dipolar polarization to enhance the dielectric constant of polymers while having low dielectric losses.

To utilize dipolar polarization, we should be aware of several strategies together with certain caution. First, normal ferroelectric polymers should be avoided for film capacitor applications because of their high hysteresis losses (>80–90% loss). Typical examples include odd-numbered nylons, poly(vinylidene fluoride) (PVDF) and its random copolymers with trifluoroethylene (TrFE), tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), and hexafluoroisopropylene (HFIP). Instead, relaxor ferroelectric polymers showing narrow double or single hysteresis loops are promising for high energy density and low loss polymer dielectrics. Because of the formation of nanosized ferroelectric domains (or nanodomains) in isomorphic crystals, high dielectric constants in the range of 30–70 can be achieved with fairly low hysteresis loss. Typical examples of relaxor ferroelectric polymers are electron beam-rotate in the glassy polymer matrix, it is highly desirable to nonpolar polymer matrix has been limited to below 1 due to a ionic polarizations are not desirable for isomorphic crystals, high dielectric constants in the range of 12–50.

In both blending and labeling of dipolar molecules, the increase in dielectric constant (or dielectric relaxation strength) for the nonpolar polymer matrix has been limited to below 1 due to a low content of the dopant molecules. Instead of using large dipolar molecules, which are difficult to rotate in the glassy polymer matrix, it is highly desirable to attach small dipolar groups to polymer chains in order to achieve easy dipole rotation. Two ways have been explored, namely, main-chain and side-chain dipoles. When dipolar groups, such as −F and −CN, are directly attached to the main-chain polymers, limited enhancement in dielectric constant and relatively high dielectric loss are observed due to the difficulty in rotating main-chain dipoles. When dipolar groups are attached in the side chains, easier rotation of the side groups can substantially increase the dielectric constant while keeping the dielectric loss relatively low. For example, when −CH2CN groups were attached as the side chains in a bisphenol A polycarbonate (i.e., CN-PC), the dielectric constant increased to 4.0 for CN-PC as compared to that of 2.9 for neat PC at 1 kHz. The dielectric loss was reasonably low, namely, tan δ = 0.005 at 130 °C and 1 kHz. Furthermore, cyanoethylated poly(2,3-dihydroxypropyl methacrylate) (CN-2-PDMA) exhibited a relatively high dielectric constant (ca. 8) between the β (rotation of −CH2CN diapoles at −60°C) and the α (Tg at 25°C) transitions at 500 Hz. However, the window between the β and α transitions was only 85°C, which is not broad enough for practical applications such as film capacitors.

To enable practical film capacitor application, it is desirable to further enhance the dielectric constant (above 10) and broaden the window between the sub-Tg transitions (e.g., above 200°C). This is achieved by blending or molecular (covalent) labeling. Note that these relaxor ferroelectric polymers showing narrow double transitions. The high Tg can prevent losses from electronic and ionic conductions, and the sub-Tg transition due to dipole rotation will enhance the dielectric constant. The temperature difference between the Tg and the sub-Tg transitions needs to be large enough to ensure a broad window for practical applications. One strategy is to dope a glassy polymer with dipolar molecules via either simple blending or molecular (covalent) labeling. Note that these large dipole moment molecules often have high nonlinear optical responses. For simple blending, the content and molecular size of the dopant molecules are important. First, the content of the dopant molecules shall be low enough to avoid macrophase separation. Even at a few percent of the dopant molecules, the Tg of the polymer matrix will significantly decrease due to the plasticization effect. Second, when the molecular size is larger than 0.6 nm, the dopant molecules will have difficulty to rotate in the glassy polymer matrix. As a result, the sub-Tg transition due to the rotation of dopant molecules often overlaps with the glass transition of the polymer matrix. For molecular labeling, the dipolar monomers are copolymerized into the backbone of a glassy polymer. Again, because of the large size and small fraction of the labeling cophomer, the sub-Tg transition from rotation of dipolar side chains is located fairly close to the glass transition. In both blending and labeling of dipolar molecules, the increase in dielectric constant (or dielectric relaxation strength) for the nonpolar polymer matrix has been limited to below 1 due to a low content of the dopant molecules.

Scheme 1. Synthesis of the Dipolar Glass Polymer, PMSEMA
chloride was added to the mixture dropwise. The reaction was slowly warmed up to room temperature over 24 h. After the reaction, triethylamine hydrochloride was removed by filtration. The remaining solvent was removed using reduced pressure distillation. The crude product was redissolved in DCM and precipitated into diethyl ether, and the dissolution–precipitation process was repeated for three times. Finally, the as-prepared monomer was dried in a vacuum oven at ambient temperature. A total of 64 scans were recorded at a resolution of 4 cm⁻¹ using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. A temperature of 150 °C was used as the standard for conventional reflection infrared (RTIR) spectra. Net signal background was obtained using the baseline (0 s, 3H, −C(CH₃)₂), 2.99 (s, 3H, −SO₂CH₂), 3.38 (t, 2H, −SO₂CH₂CH₂O−), 4.62 (t, 2H, −SO₂CH₂CH₂O−), 5.65 (s, 1H, −C(CH₃)₂=CH₂), 6.14 (s, 1H, −C(CH₃)₂=CH₂), 13.56 (s, 1H, −C(CH₃)₂=CH₂), 134.0 (C(CH₃)=CH₂), 159.0 (−OCOC(CH₃)₂). FTIR spectra were obtained using pellets prepared by grinding solid samples with potassium bromide (KBr) powder.

The density measurement for PMSEMA was carried out by the suspension method. First, the PMSEMA was hot-pressed into a bubble-free film. Then, it was placed into a glass vial with mixed diethyl ether (density of 0.713 g/cm³) and chloroform (density of 1.48 g/cm³). After sonication to remove surface bubbles, the film was suspended in the mixed solvent by adjusting the ratio of diethyl ether to chloroform. The suspension should be stable for at least 1 h. The density of the mixed solvent was taken as the density of the PMSEMA film.

Broadband dielectric spectroscopy (BDS) measurements were performed on a Novocontrol Concept 80 broadband dielectric spectrometer with temperature control. The applied voltage was 1 Vrms (rms means root-mean-square) with the frequency ranging from 0.01 Hz to 10 MHz and the temperature from −150 to 120 °C. Silver electrodes (100 nm thick) were evaporated by electron beam (EvoVac Deposition System, Angstrom Engineering Inc.) onto Kapton films, which was often used as a strong flexible backing to survive hot-press at high temperatures (up to 250 °C). The electrode area was ca. 0.786 cm². The dried PMSEMA powder was sandwiched between two Kapton films with silver electrodes and then hot-pressed at 150 °C into 174 μm thick bubble-free films for BDS measurements.

The electric displacement-electric field (D–E) hysteresis loop measurements were carried out using a Premiere II ferroelectric tester (Radiant Technologies, Inc.) equipped with a Trek 10/10B-15 high voltage amplifier (0–10 kV AC). The applied voltage had a bipolar sinusoidal waveform ranging from 10 to 2000 Hz. The sample was immersed in a silicone oil bath during tests, and the temperature was varied from 25 to 75 °C. The temperature was controlled using an IKA RCT temperature controller. The hot-pressed PMSEMA (about 50 μm thick) sandwiched between two silver electrode-coated Kapton films were prepared similarly to those for the BDS measurements, except that the electrode area was ca. 0.0515 cm². For the solution-cast film, the PMSEMA solution in redistilled DMF (20 mg/mL) was drop-cast onto a Kapton film coated with Ag electrode. The sample was dried at ambient temperature for 2 days and then at 110 °C in a vacuum oven for 4 days. The film thickness was around 26.1 μm.

Note that Kapton films were outside of the Ag electrodes, which were directly connected to an external cathode and anode. Therefore, the Kapton film would not affect the BDS and D-E loop measurements of the sample. This sample preparation method was verified for known polymer samples, such as PS and poly(methyl methacrylate) (PMMA); see Figure S1 in the Supporting Information. The measured dielectric constants for the hot-pressed PS and PMMA samples were 3.0 (by BDS) and 3.3–4.0 (by D-E loop), respectively, similar to the literature values for PS (2.6–3.0) and PMMA (2.8–4.3).31

3. RESULTS AND DISCUSSION

Scheme 1 shows the synthesis of PMSEMA from MSEM via conventional free radical polymerization initiated by
AIBN in DMF at 60 °C. The MSEMA monomer was synthesized by reacting the 2-(methylsulfonyl)ethanol with methacryloyl chloride in DCM in the presence of Et3N. The structure of the purified MSEMA was confirmed by 1H and 13C NMR spectroscopy and had a melting point of 49 °C. Polymer molecular weight was measured by SEC using DMAc as the solvent and PS standards for conventional calibration. A symmetric unimodal peak was observed. The number-average molecular weight was 58 000 g/mol, and the molecular weight distribution was 3.1. Although this molecular weight appears relatively low for good mechanical properties, the dielectric constant and polarization of a polymer are not much influenced by its molecular weight. In the future, we will optimize our synthesis for higher molecular weight samples and study their mechanical and rheological properties. Note that high molecular weight and optimal rheological properties are required for biaxial stretching of amorphous polymers (e.g., PS) in order to obtain thin film thickness (ca. 10 μm). The PMSEMA was soluble in polar solvents such as DMF and dimethyl sulfoxide (DMSO), but not in acetone, diethyl ether, tetrahydrofuran (THF), chloroform, or toluene. Figure 1A,B shows 1H and 13C NMR spectra of purified PMSEMA. By comparing the 1H and 13C NMR spectra of PMMA,32 all protons and carbons in the repeat unit can be successfully assigned. Main-chain protons and carbons showed multiple peaks due to random tacticity. Neat PMSEMA was an amorphous polymer and showed a Tg around 109 °C at a heating rate of 10 °C/min (see Figure 2A). Due to strong dipolar interactions among sulfone side groups, this Tg was much higher than that for an analogue polymer, poly(n-butyl methacrylate) (PnBMA, Tg = 20 °C), but similar to that for PMMA (Tg = 105 °C). The TGA result in Figure 2B showed that 5 wt % degradation started around 270 °C, above which two-step degradation processes were seen. The first step

Figure 2. (A) DSC and (B) TGA curves for PMSEMA. The DSC and TGA heating rates are 10 and 20 °C/min, respectively. The inset in (B) shows FTIR spectra for PMSEMA before and after being heated under a dry N2 atmosphere in TGA.

Figure 3. (A) Real (ε′) and (B) imaginary (ε″) parts of relative permittivity and (C) dissipation factor (tan δ) as a function of temperature at different frequencies for PMSEMA. (D) ε′, (E) ε″, and (F) tan δ as a function of frequency at different temperatures for PMSEMA.
The dipole moment of the sulfonyl group is 4.25 D. The dipole moments for the ester group is 1.75 D. If we assume the side chain atoms are in an all trans conformation, the total dipole moment of the MSEMA repeat unit would be about 6.0 D, if the ester and sulfone groups can align parallel. From calculation, the \(-\text{OCH}_2\text{CH}_2\text{SO}_2\text{CH}_3\) side chain occupies about 65 wt % of a repeat unit. We speculate that the first step degradation was thermal cleavage of the \(-\text{OCH}_2\text{CH}_2\text{SO}_2\text{CH}_3\) side groups. This was proved by FTIR results for PMSEMA before and after being heated to 390 °C. Note that similar transitions are also observed for polymethacrylates with long alkyl side chains such as isobutyl and n-butyl groups. However, these transitions are fairly weak due to the weak polarity of the long alkyl side chains. Ideally, direct and accurate assignment of the \(\beta\) and \(\gamma\) transitions can only be achieved by solid-state multidimensional \(^1\text{H}\) NMR, which is similar to the work performed for PMMA in ref 34. In the future, we will pursue this effort through potential collaborations.

From this BDS result, we can define the glassy PMSEMA between \(-80\) and \(90\) °C as a dipolar glass polymer, rather than a paraelectric polymer. As we discussed in ref 1, both dipolar glass and paraelectric polymers show a more or less linear D-E hysteresis loop before dipole saturation. However, the dipole–dipole interaction is weaker in a dipolar glass polymer than in a paraelectric polymer. Consequently, a dipolar glass polymer will exhibit a lower dielectric constant (or dipolar polarization) than a paraelectric polymer. This is exactly seen for PMSEMA in Figure 3A. Below the \(T_g\) around \(94\) °C, the dielectric constant of glassy PMSEMA is about \(11.4\) at room temperature and \(1\) Hz. Above the \(T_g\), the dielectric constant of molten PMSEMA is as high as \(36.6\) at \(1\) Hz. Obviously, the translational motion in addition to the rotational motion of the molecular dipoles in the polymer melt enhances the dipole–dipole interaction. Therefore, we conclude that the glassy PMSEMA between \(-80\) and \(90\) °C is a dipolar glass polymer, whereas molten PMSEMA above \(100\) °C is a paraelectric polymer.

Figure 3D,E shows frequency-scan results at different temperatures. Between \(-120\) and \(60\) °C, \(\varepsilon'_r\) gradually decreased with increasing frequency; this could be attributed to the relaxation of sulfone dipoles. Corresponding dipole dispersion peaks in \(\varepsilon''_r\) were observed at different temperatures, e.g., \(6.5\) Hz at \(-90\) °C, \(1.15\) kHz at \(-60\) °C, \(36.5\) kHz at \(-30\) °C, \(487\) kHz at \(0\) °C, and \(1.78\) MHz at \(30\) °C. Obviously, the peak frequency increased with increasing temperature. Above \(90\) °C,
contribution from impurity ions started to be seen in Figure 3D,E, because both $\varepsilon_r'$ and $\varepsilon_r''$ increased with decreasing frequency. In other words, ionic polarization could be ignored when the temperature was below 75 °C and the dielectric constant increase could be attributed to the dipolar polarization. $\varepsilon_r''$ versus frequency had a slope of $-1$ below 10 Hz in the double logarithmic plot. For polar polymers, trace amounts of impurity ions are difficult to avoid, and even sub-ppm levels of impurity ions could cause a significant loss.37−39 Because of the dipole motions, $\varepsilon_r'$ reaches about 11.4 at 25 °C and 1 Hz, together with a reasonably low dielectric loss, i.e., tan δ = 0.02. The window between $\gamma$ (ca. −110 °C) and $\alpha'$ (94 °C) transitions is as large as ca. 204 °C. In addition, the $\gamma$ dipole relaxation takes place at a high frequency of ca. 1 MHz around room temperature. All of these dielectric properties suggest that PMSEMA shall be a good candidate for room temperature, high dielectric constant, and low loss dielectric film capacitor applications.

The activation energy for the $\gamma$ transition could be estimated by the Arrhenius equation from both temperature- and frequency-scan BDS results in Figure 3,33 and results are shown in Figure 4A,B, respectively. The activation energy was determined to be 0.50 ± 0.02 and 0.56 ± 0.02 eV for temperature- and frequency-scan BDS results. These activation energy values for the $\gamma$ transition were considerably lower than those reported for the $\beta$ transitions in polymethacrylates with methyl, ethyl, and $n$-butyl groups, i.e., ca. 0.83 eV.35 Assuming the ester group had the same activation energy as those in polymethacrylates, our result indicated that the rotation of the sulfone groups was easier than the ester groups in the side chains of PMSEMA. It is considered that the size of sulfone groups is small enough so that they can more easily rotate in the free volume of the glassy polymer matrix. Currently, there has been no available theoretical prediction for orientational polarization for side-chain polar polymers. In order to understand how much percentage of sulfone dipoles can rotate with a random orientation, we estimate the theoretical polarization, $P_{\text{dip, theory}}$, using the Langevin equation for freely rotating polar molecules8,9,28

$$P_{\text{dip, theory}} = N \mu RU \left( \coth \frac{u}{\theta T} - \frac{1}{u} \right)$$

(1)

where $N$ is the repeat unit density ($N = 4.36 \times 10^{27}/m^3$ for PMSEMA), $\mu RU$ the dipole moment of the repeat unit ($\mu RU$ is 4.25 D for the sulfone group only and 6.0 D for combined sulfone and ester groups), $E$ the applied electric field, $k_B$ the Boltzmann constant, and $T$ the absolute temperature. At $E = 100$ MV/m, theoretical $P_{\text{dip, theory}}$ values for PMSEMA at −50
and 50 °C are calculated to be 9.48 and 18.0 mC/m², respectively. Here, we consider that only sulfone groups polarize at −50 °C (μRU = 4.25 D) and both sulfone and ester groups polarize at 50 °C (μRU = 6.0 D). Experimental polarization (P_dip,exp) due to dipolar motion for PMSEMA can be estimated as:

\[ P_{\text{dip,exp}} = P_T - P_{-150 \degree C(1 \text{ MHz})} \]
\[ = [\varepsilon_{r,T} - \varepsilon_{r,-150 \degree C(1 \text{ MHz})}]\varepsilon_0E \tag{2} \]

where \( P_T \) and \( P_{-150 \degree C(1 \text{ MHz})} \) are polarizations, and \( \varepsilon_{r,T} \) and \( \varepsilon_{r,-150 \degree C(1 \text{ MHz})} \) are relative permittivity from BDS results at \( T \) and −150 °C, respectively. At −150 °C and high frequency (e.g., 1 MHz), we consider that the dielectric contribution to permittivity only originates from electronic and vibrational polarizations, and \( \varepsilon_{r,-150 \degree C(1 \text{ MHz})} = 5.0 \). Assuming the electronic and vibrational polarizations are nearly independent of temperature, 940 the \( P_{\text{dip,exp}} \) values at 100 MV/m for PMSEMA at −50 and 50 °C (1 Hz) are calculated to be 3.72 and 6.64 mC/m², respectively. Considering that the ratio of \( P_{\text{dip,exp}}/P_{\text{dip,theory}} \) may represent the percentage of dipole flipping, the ratios are 39% and 37% at −50 and 50 °C, respectively. The similar \( P_{\text{dip,exp}}/P_{\text{dip,theory}} \) ratios at −50 and 50 °C further confirm our earlier conclusion that the strong γ transition is only due to the polarization of sulfone groups and the weak β transition originates from the combined polarization of sulfone and ester groups. Both ratios are significantly higher than that (10%) reported for the CN-PC,29 suggesting that sulfone and/or ester groups are more advantageous than the −CH₂CN groups in enhancing the dielectric constant of polymers.

The above studies focus on dielectric properties at low electric fields. In real dielectric applications, high electric fields are usually applied. High electric field dielectric properties were first studied by D-E hysteresis loop measurements for the hot-pressed PMSEMA film (42.5 μm thick). Centered bipolar D-E loops are shown in Figure 5. At 25 °C, narrow linear D-E loops were observed up to 182 MV/m from 20 to 2000 Hz. From the slope of these linear D-E loops, the apparent \( k \) could be determined as \( k = D/\varepsilon_0E \). Alternatively, the dynamic relative permittivity \( k' \) can also be defined as \( k' = D/\varepsilon_0E \). As we can see from Figure S2 in the Supporting Information, \( k \approx k' \) within the ±200 MV/m range. This suggests that the nonlinearity for PMSEMA at 20 Hz and 25 °C can be negligible. It was observed that \( k \) values slightly increased with increasing the poling field or decreasing the poling frequency. For example, at 182 MV/m, \( k = 11.8 \) at 2000 Hz and 12.4 at 20 Hz. These \( k \) values were generally consistent with those in the above BDS results. When the temperature was increased to 50 °C (Figure 5G), relatively narrow and linear D-E loops were still observed, with slightly decreased maximum poling field and increased loop hysteresis, especially for 20 Hz. This could be attributed to enhanced dipole switching and certain impurity ion migration as the temperature approached the glass transition. Note that fresh samples were used for each poling frequency until a maximum poling field was reached. It was the different quality in each fresh hot-pressed sample that caused different maximum poling fields in Figure 5. These maximum poling fields cannot be simply considered as the Weibull breakdown strength. We also note that the hysteresis loss for PMSEMA at 75 °C is much lower than those for e-beamed P(VDF-TrFE) and P(VDF-TrFE-CFE) at the same temperature (see Figure S5 in the Supporting Information).
ref 38). This could be attributed to high ionic and electronic conduction in the high temperature paraelectric phases for P(VDF-TrFE)-based random copolymers. From these results, we concluded that the high dielectric constant and low loss dielectric properties persisted into high electric fields and they could again be attributed to the dipolar polarization of strong sulfone dipoles in PMSEMA.

In addition to the hot-pressed film, a solution-cast PMSEMA film (261 μm) was also obtained by drop-casting from redistilled DMF. Bipolar D-E loops of the solution-cast PMSEMA film and a commercial PMMA film (49 μm) at 25°C and 20 Hz are shown in Figure 6. Due to a thinner film thickness and better film quality, the solution-cast PMSEMA film exhibited a higher maximum poling field, up to 283 MV/m, as compared to the hot-pressed PMSEMA film in Figure 5. Above 180 MV/m, the tips of the D-E loops slightly tilted up, possibly due to flipping of additional sulfonyl dipoles which were originally difficult to rotate in the sample. Note that the $\frac{P_{\text{dip,exp}}}{P_{\text{dip,theory}}}$ ratio was about 37%, indicating that not all dipoles had responded to the external electric field. This could be attributed to the random orientation of methylsulfonyl groups and/or not large enough free volume in the glassy PMSEMA. At a high enough electric field, these difficult-to-rotate dipoles started to rotate, resulting in a further increase in the total $D$ value. For comparison, bipolar D-E loops for a commercial PMMA film are shown in Figure 6B. PMMA exhibited a lower $k$ value of ca. 4.5 at room temperature, and the loops were somewhat broader than those for the solution-cast PMSEMA film. It was reported that the $\beta$ transition of PMMA was located around 25°C at 1 Hz. Therefore, the broadening in its D-E loops could be attributed to the methyl ester dipole relaxation in PMMA around room temperature.

The stored ($U_{\text{stored}}$) and discharged ($U_{\text{discharged}}$) energy densities can be obtained from D-E loops and are compared for PMSEMA and PMMA in Figure 6C. Solution-cast and hot-pressed PMSEMA films exhibited similar discharge energy densities, although the charged energy density was slightly higher for the solution-cast PMSEMA film. Obviously, the discharge energy density for PMSEMA was much higher than that for PMMA at the same poling electric field. For example, at 200 MV/m, PMSEMA had a discharge energy density of 2.18 J/cm$^3$, which was 3.2 times that of PMMA, while the loss %, defined as 100(1 $- U_{\text{discharged}}/U_{\text{stored}}$), for PMMA was much higher than those for the solution-cast and hot-pressed PMSEMA films (see Figure 6D). This again could be attributed to dipole switching during the $\beta$ transition around room temperature for PMMA. Because the $\gamma$ transition for PMMA was around $93{°}$C at 20 Hz, the losses for PMSEMA were lower than that for PMMA. Note that the loss for the solution-cast PMSEMA film was slightly higher than that for the hot-pressed PMSEMA film, which might be attributed to the different film preparation methods. For example, the solution-casting method might introduce additional residue solvent (DMF) and impurity ions in the sample, which could eventually increase the dielectric loss. Actually, we have run $^1$H NMR for the PMSEMA sample, but could not detect any trace of DMF within the instrument limit, indicating that the content of residue solvent must be less than 0.1–0.5% (i.e., about the $^1$H NMR limit). On the basis of our recent studies on PVDF and its copolymers, even ppm levels of impurity ions can cause significant dielectric loss. It is probable that the residue content could be around the ppm level in solution-cast PMSEMA. Note that such a small amount of residue impurity will not substantially decrease the breakdown strength of polymer films. For example, biaxially stretched PVDF films, which usually contain ppm levels of impurity ions inherited from suspension polymerization, still shows a high DC breakdown strength greater than 700 MV/m.45

4. CONCLUSIONS

In summary, we have demonstrated a model dipolar glass polymer, PMSEMA, which exhibited a high permittivity (11.4 at 1 Hz and 10.5 at 1 kHz) and relatively low loss (tan $\delta \sim 0.02$) at room temperature. Due to strong dipolar interactions, the glass transition of PMSEMA was at 109°C, much higher than the $T_g$ (ca. 20°C) of the analogue polymer, PnBMA. Due to the small size and large dipole moment (4.25 D) of the side-chain sulfone groups, a strong $\gamma$ transition was observed at ca. $-110{°}$C. This strong $\gamma$ transition increased the dielectric constant of PMSEMA from ca. 5.0 at $-150{°}$C (at 1 MHz) to 9.2 at $-50{°}$C (at 1 Hz). Considering the nature of the $\beta$ transition in polymethacrylates with alkyl side chains (i.e., the rotation of the ester side groups between 10 and 60°C at 1 Hz), a weak $\beta$ transition was assigned between 0 and 60°C for combined polarization of sulfone and ester dipoles in PMSEMA. Due to this $\beta$ transition, the dielectric constant further increased to 12.5 at $50{°}$C at 1 Hz. From frequency-scan BDS, the relaxation of sulfone dipoles was as fast as $\sim 1\mu$s at room temperature. The dipole switching percentage of the sulfone groups was estimated as high as 37–39% in PMSEMA, much higher than that in $-\text{CH}_2\text{CN}$ containing polymers. D-E loop studies indicated that the high dielectric properties persisted to high electric fields. The discharged energy density was nearly 3 times that of PMMA, whereas the dielectric loss was only 1/3–1/2 of that of PMMA. These experimental results suggest that PMSEMA is a good candidate for high energy density and low loss polymer dielectric at room temperature.

However, there are still opportunities to further improve dielectric properties of a dipolar glass polymer, such as PMSEMA. First, uniaxial stretching should be further increase dipolar polarization and thus the dielectric constant of PMSEMA, because uniaxial alignment of polymer chains will facilitate dipole rotation in the side chains. A similar orientational effect on dielectric constant is seen for PVDF and PVDF-graft copolymers. Second, the number of CH$_2$ groups between the sulfone and ester groups can be varied to find the optimal dielectric properties. We expect that one CH$_2$ group between sulfone and ester groups may further increase the $T_g$ and enhance the coupling between the sulfone and ester groups. On the contrary, more than two CH$_2$ groups will decrease the $T_g$ and thus decrease the temperature window between the $\gamma$ and $\alpha$ transitions. Third, the dissipation factor of 0.02 is still considered high for practical electrical and power applications. From the lesson of the methyl ester group rotation in PMMA, we speculate that the free volume might not be large enough to allow friction free rotation of sulfone dipoles. Therefore, it is desirable to slightly increase the free volume in dipolar glass polymers. Fourth, to obtain high $T_g$ values (e.g., above 150°C), the main-chain rigidity must be increased in order to avoid a potential decrease in $T_g$ due to the increase in free volume of the glassy polymer. This requires utilization of rigid-rod backbone polymers such as polyimides. Research is currently underway to develop better dipolar glass polymers to achieve high energy density and high temperature capability while maintaining low dielectric losses.
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